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(54) PROCESS FOR THE TREATMENT OF A METAL SURFACE AND A METHOD OF MANUFACTURING DRESSED STEEL PLATE USING THE PROCESS

(71) We, SUMITOMO METAL INDUSTRIES LIMITED and IGETA STEEL SHEET CO. LTD., both Japanese corporations of respectively, 15, 5-chome, Kitahama, Higashi-ku, Osaka City, Japan, and 2, Dejima, Nishimachi, Sakai City, Japan, do hereby declare the invention for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of treating the surface of steel plate which conveniently and inexpensively provides steel plates for painting, dressed steel plates and dressed steel foils which are inexpensive and excellent in rust-resisting property and readily painted, particularly dressed steel plate dressed with diallyl phthalate resin impregnated paper, without using any adhesive.

Heretofore, the rust proofing of steel plates has usually been effected by using rust proofing oil. However, the rust proofing oil has to be removed when the plate is to be painted or printed. Also, grease removing treatment and treatment with phosphate are carried out on steel plate that is to be painted. The treatment of steel plate with phosphate has heretofore been made by the following methods:

(a) "Aqueous solution method", in which the steel plate is treated by using an aqueous solution containing orthophosphoric acid, polyphosphoric acid and one or more salts theref and also such additive as an oxidizing agent.

(b) "Dry method", in which the steel plate is treated with an organic solvent such as trichloroethylene and low grade alcohols.

According to these methods, the film forming function is low, requiring over ten seconds as the reaction time, so that it is impossible to produce steel plate suitable for painting in the form of steel strip continuously and at high speed, which plates yet have sufficient rust proofing and adaptability for painting.

To solve this problem, use has been made of electrolytic chromic acid treated steel plates and zinc electroplated steel plates. However, the former are expensive and do not readily bond with paint, while the latter do not have sufficient surface smoothness. Therefore, neither method is satisfactory.

Also, in the manufacture of dressed plates by laminating steel plate or steel foil with diallyl phthalate resin impregnated paper, it has been the practice first, completely to remove fatty matter such as rust proofing oil and stains before bonding the steel plate or foil and impregnated paper with adhesive intervened therebetween by means of a thermal press. However, if the bonding process is effected without using any adhesive, the steel plate or foil and impregnated paper would hardly be bonded together, or the bond obtained would be too weak to withstand practical use.

For the treatment of metal surfaces, there have been proposed various methods using a treating agent obtained by adding either phosphate or chromate or both of them to organic macro-molecular compounds. For example, it has been proposed to coat metal with an aqueous dispersion containing a hydrophobic resin, for instance a mixture of butadiene-styrene copolymer and chromium compound, or with a solution containing an ammonium salt or amine salt of a copolymer containing acrylic acid or methacrylic acid and low grade alkyl esters thereof and a water soluble compound of chromate, or with an aqueous solution containing a partial phosphate ester of polyvinyl alcohol, or with a treatment liquid chiefly composed of an emulsion of a water dispersive organic macro-molecular compound, for instance an acrylic acid copolymer emulsion, a water soluble chromium compound and phosphoric acid ions.

In any of the above metal surface treatment methods, however, immersion for a long

time and/or fixing at high temperature for a long time are indispensable, thus requiring high equipment cost. Therefore they are unsuitable for treating ground treated steel plate, particularly steel strip, continuously and at high speed.

According to the invention there is provided a method of treating a steel surface, comprising applying a film to the said steel surface of a composition comprising at least one inorganic acid selected from phosphoric acid or its salt, polyphosphoric acid or its salt, chromic acid or its salt, an organic macromolecular compound stable in an acidic medium, and a non-aqueous vaporizable solvent, and thermally drying the coated steel surface at a temperature in the range 65° to 150°C for from 2 to 10 seconds, and wherein said composition comprises 10 to 30 wt. % of the said inorganic acid(s) or salt(s) and 5 to 35 wt. % of the said organic macro-molecular compound.

The solvent employed may be an alcohol or a ketone.

The film is uniformly and thinly coated over the steel plate or strip by such means as roller coating or spraying, immediately followed by the thermal drying, e.g. with hot air at 65° to 150° for from 2 to 10 seconds, whereby ground treated steel plates for coating and steel plates and strips for dressing are produced in a simple process, inexpensively, at high speed and continuously.

A second object of the invention is to provide a method of producing dressed steel plates or dressed steel foils by bonding thermosetting resin impregnated paper to the aforementioned pre-treated steel plates or foils without using any adhesive.

The content of one or more members of the group consisting of phosphoric acid, polyphosphoric acid, chromic acid and salts of these acids in the coating liquid ranges between 10% and 30% by weight. With a content below this range, the bonding property is inferior. On the other hand, with a content in excess of the range the liquid is prone to precipitation due to gellation, that is, the stability is degradated, which is undesired.

Also, the content of the stable organic macro-molecular compound, for example a polymer which may be polyvinyl butyral resins and acryl latex in the acidic solution, ranges between 5% and 35% by weight. With a content below this range the rust proofing property and bonding property are inferior. On the other hand, exceeding this range is undesired because no improvement is obtained and cost is increased.

Now, some examples of the invention will be given.

Example 1.

A film composed of 10% by weight of polyvinyl butyral resin, 15% by weight of lead trimethylate, 5% by weight of zinc polyphosphate, 7% by weight of lead chromate, 50% by weight of ethanol and 1% by weight of a surface active agent, the rest being water, was applied by a roller over a cold rolled steel plate 0.4 mm in thickness previously washed to remove grease. Then, the coated steel plate was dried with hot air at 80°C for 5 seconds, thus forming a pre-treated steel plate. The thickness of the dry coating was 1.3 to 1:5 microns. The coating was colourless, transparent and very smooth.

Table 1 shows the processibility, rust proofing property and painting property of the treated steel plate treated according to the invention and that which is treated according to a prior-art method using an organic macromolecular compound.

It will be seen from Table 1 that the treated steel plate treated according to the invention has superior properties.

TABLE 1

A: Steel plate treated according to the invention

B: Steel plate treated according to a prior-art method using an organic macre-molecular compound

	Treatment condition	Rust proving property (by exposure in outdoor for 9 months)	Painting property (acryl resin 20-micron painting) Checkerboard cellophane tape peel-off test	Checkerboard cellophane tape peel-off test after wetting test	Checkerboard cellophane tape peel-off test after immersion in 3-% table salt water
A	Dried at 65 to 150°C for 2 to 10 seconds	The surface assumed slightly brownish color in 30 days	Satisfactory	Satisfactory	Slightly peeled off
B	Dried at 250 to 300°C for 45 seconds	Rust was recognized in 20 days	Satisfactory	Satisfactory	Peeled off

Example 2.

Diallyl phthalate resin impregnated paper was placed on the pre-treated steel plate treated in Example 1 as the base, and the two were bonded together with a thermal press at a temperature of 130 to 140°C and with a pressure of 10 to 12 kg/cm² for 7 minutes. Table 2 shows the results of bond tests conducted on the dressed steel plate obtained according to the invention and comparison dressed steel plates obtained by other methods. The test was made by immersing the plate in a hot water at 70°C, followed by drying at a temperature of 60°C for 3 hours, and observing the state of peel from the edge. The grease removal for the bare steel plate shown in the Table was carried out by the alkali spray method.

TABLE 2.

Steel plate	Bonding property
Steel plate treated according to the invention	Not peeled
Bare steel plate coated with adhesive	Not peeled
Steel plate treated with zinc phosphate	Partly peeled
Bare steel plate	Totally peeled

It will be seen from the above test result that the treated steel plate treated according to the invention has the same excellent bonding property as that of the steel plate coated with adhesive.

Example 3.

The treatment agent used in Example 1 was applied by the immersion method over a steel foil 50 microns in thickness washed for grease removal, followed by drying with hot air at 80°C for 5 seconds, thus obtaining a pre-treated steel foil. The thickness of the dry coating was 1.3 to 1.4 microns.

Then, the impregnated paper was bonded to this pre-treated steel foil as the base in the same way as in Example 2. Table 3 shows the results of bond tests conducted on the dressed steel foil obtained in this example and a bare steel foil coated with adhesive by the same test method as in Example 3. The grease removal for the bare steel foil shown in the Table was done by the trichloroethylene immersion method.

TABLE 3.

Base	Checkerboard plus cellophane tape	Knife-cut plus 180-degree bending
Steel foil treated according to the invention	Not peeled	Not peeled
Bare steel foil coated with adhesive	Not peeled	Not peeled

It will be seen from the above test results that excellent bonding property can be obtained according to the invention even in the case of the steel foil.

WHAT WE CLAIM IS:—

1. A method of treating a steel surface, comprising applying a film to the said steel surface of a composition comprising at least one inorganic acid selected from phosphoric acid or its salt, polyphosphoric acid or its salt, chromic acid or its salts, an organic macro-molecular compound stable in an acidic medium, and a non-aqueous vaporizable solvent, and thermally drying the coated steel surface at a temperature in the range 65° to 150°C for from 2 to 10 seconds, and wherein said composition comprises 10 to 30 wt. % of the said inorganic acid(s) or salt(s) and 5 to 35 wt. % of the said organic macro-molecular compound.

2. A solvent according to claim 1 or 2, wherein said solvent is an alcohol or a ketone.

3. A method according to either of claims 1 or 2, wherein the said composition is coated over at least one surface of the steel to a thickness of 1.1 to 1.5 microns.

4. A method of treating a steel surface according to claim 1, substantially as hereinbefore described with particular reference to the Examples.

5. Steel surfaces treated by a method according to any of claims 1 to 4.

6. A method of manufacturing a dressed steel plate comprising applying to a treated surface accordin to claim 5 a thermosetting resin-impregnated paper and bonding the paper to the steel by means of a heating step.

7. A method according to claim 6, wherein said thermosetting resin-impregnated paper is a diallyl phthalate resin-impregnated paper.

8. A method of manufacturing a dressed steel plate according to claim 6, substantially as hereinbefore described with particular reference to the Examples.

9. A dressed steel plate obtained by a process according to any of claims 6 to 8.

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